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(54) Title: LINEAR, ISOTACTIC POLYMERS, PROCESS FOR PREPARING SAME, AND USE THEREOF

(57) Abstract

Linear, isotactic polymer which has a structure of one or several C_2 to C_{20} olefins and, of which the isotacticity is within the range of from 25 to 60 % of [mmmm] pentad concentration, the polymer having a mean molecular weight Mw within the range of from 100.000 to 800.000 gms/mol and a TG of from -50 to +30.

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Linear, Isotactic Polymers, Process For Preparing Same, And Use Thereof

The present invention relates to linear, isotactic polymers, to a process for preparing same, and to the use thereof, isotacticity of the linear polymers, due to a statistic distribution of stereoscopic errors in the polymer chain, being within the range of from 25 to 60 % of [mmmm] pentad concentration.

For a long time, isotactic polymers have been of interest as plastic materials for manufacturing articles of relatively good deformation resistance, such as e.g. sheathings of household appliances. In general, such isotactic polymers with propylene as monomer are of highly crystalline nature and, therefore, relatively hard with little or no impact resistance at all so that they will come into question only for application fields in which those characteristics are desirable.

Most recently, various attempts have been made, aiming at preparing also polypropylene with elastic characteristics. European Printed Publication 0 707 016 A1 specifies a catalyst composition and a process for preparing polyolefins. The catalysts specified in European Printed Publication 0 707 016 A1 are, in substance, made up of a metallocene compound having an indene ring and a fluorene ring which are bridged via C, Si or Ge. In case of the metallocene compound, it, in this connexion, is obviously essential that, in the indene ring system, at least the residue denoted with R^4 not be hydrogen. When that residue R^4 is hydrogen, the effects, such as specified in the aforementioned European Patent Application, will not be attained (P 6, from L 57 up to P 7, L 3). The polymers specified in European Printed Publication 0 707 016 A1 and prepared with metallocenes, here especially the polypropylene prepared with those metallocenes, however, show as can be drawn from the examples and the graphs, but unsatisfactory characteristics in regard of the elastic behaviour.

Departing from all these facts, it is the object of the present invention to make polymers from olefinically unsaturated compounds available, not only showing thermoplastic but, at the same time, thermoplastic-elastic characteristics and, thus, being applicable for many application fields. It is a further object of the present invention to suggest a process suitable therefor and serving for preparing the polymers and to particularise the use thereof.

That object is, in regard of the polymers themselves, solved by the characterising features of Claim 1; in regard of the process for preparing the polymers, it is solved by the characterising features of Claim 11, and in regard of the use, it is solved by Patent

Claim 18. The Subclaims show advantageous further developments.

According to the invention, linear, thermoplastic, elastic polymers from an olefinically unsaturated compound with an isotactic arrangement of the monomer units and a statistic distribution of isolated stereoscopic errors along the individual chains and a mean molecular weight Mw of the polymers within the range of from 100,000 to 800,000 gms/mol and a TG of from -50 to +30, thus, are suggested, binary, linear olefins which show an arbitrary or rather regular sequence of isotactic and atactic blocks being excluded.

With the polymer according to the invention, it is essential that the stereoscopic errors be situated in the polymer chain itself and that, thus, a specific pentad concentration result. In this connexion, it was found that, with the polymers according to the invention, the [rmrm] pentad with a maximum of 2.5 % of the entire pentad area will, in general, be present. In many cases, it was also found that that [rmrm] pentad was completely missing.

Furthermore, it became evident that, in most cases, the [rrrr] and [rrrm] pentads are always greater than the [rmrm] pentad. Determination of the pentad concentration in case of polymers has, properly speaking, become known from the state-of-the-art and is specified e.g. in J. A. Ewen, "Catalytic Polymerisation of Olefins", Eds. T. Keii, K. Soga; Kodanska Elsevier Pub.; Tokyo, 1986, P 271 et seqq. Also the pentad concentration determination according to the invention now present was carried out by means of the method specified in the above-mentioned piece of pertinent literature.

Apart from the above-mentioned specific pentad concentration, the linear, isotactic polymers according to the invention have a molecular weight within the range of from 100,000 to 800,000, of preference from 110,000 to 500,000 and of special preference within the range of from 120,000 to 300,000 gms/mol. The mean molecular weights Mw (mean weight value) of the polymers according to the invention were measured by means of the gel permeation chromatography (GPC) method at 135 °C with microstyragel as column material and 1, 2, 4-trichlorobenzole as solvent against closely distributed polypropylene standards. The molecular weight distribution Mw/Mn (mean weight value/mean numerical value) of the polymers according to the invention was likewise measured by means of the gel permeation chromatography method and generally amounts to from 1.2 to 3.5.

In addition to all that, the polymers according to the invention show a glass transition temperature Tg within the range of from -50 °C to +30 °C, of special preference a Tg of from -20 °C to +10 °C. The glass transition temperature was determined by means of the DSC method.

The linear, isotactic polymers according to the invention present, after all, a structure of one or several C_2 - C_{20} olefins. In this case, the olefin is preferred to be a C_3 -C_{20} - Alk-1-ene. Examples of such C_3 - C_{20} - Alk-1-ene are: propene, 1-butene, 2-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-hexadecene, 1-octadecene, 1-eicosene.

Apart from the already mentioned olefins, also C_5 - C_{20} cycloolefins are of the especially suitable kind.

Examples thereof are cyclopentene, cyclohexene, norbornadiene and its derivatives.

In case of the linear, isotactic polymers, polypropylene is especially preferred. Further suitable polymers are copolymers from propylene and a C_4 - C_{20} olefin or a cycloolefin. It is also possible to prepare terpolymers which show the characteristics defined in Patent Claim 1 when they present a structure of propylene, a C_2 - C_{20} olefin and a cycloolefin.

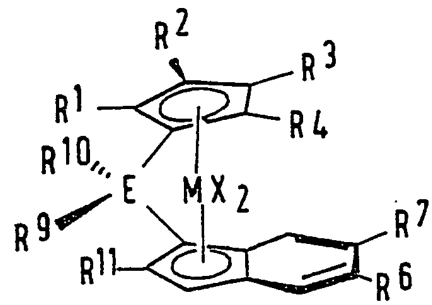
The polymers according to the invention are e.g. soluble in toluol at a temperature within the range of from 20 to 80 °C; they show a distinct elastic behaviour in a tensile-strength test, measured with a "Standard Universal Testing Machine ZWICK 1445", as specified in the examples, and, in general, possess a crystallisation melting temperature, measured by means of the "Differential Scanning Calometry" (DSC) method within the range of from -50 °C to 150 °C. In particular, it has to be emphasised that, also in this case, the polymers according to the invention clearly differ, in regard of their elastic-thermoplastic behaviour, from the state-of-the-art, i.e. from European Printed Publication 0 707 016 A1 mentioned in the introductory part to the Description. This being so, the polymers according to the invention are particularly suited for the manufacture of articles of relatively good deformation resistance, such as e. g. sheathings for household appliances. Furthermore, it is worth mentioning that the polymers can be used in polymer mixtures for impact resistance modification. Due to their elastic characteristics, the polymers are especially suited for elastic sheets, moulded bodies, and gaskets.

The invention, furthermore, relates to a process for preparing linear, thermoplastic-elastic polymers from olefinically unsaturated compounds with an isotactic arrangement of the monomer unit and a statistic distribution of isolated stereoscopic errors along the individual chains, tacticity varying within the range of between 25 and 60 % [mmmm] pentad concentration. A regular sequence of isotactic and atactic blocks, therewith, is excluded. In many cases, it was found that the [rmrm] pentad was totally missing or present with a maximum of 2.5 % of the entire pentad area. Furthermore, it became evident that, in most cases, the [rrrr] and [rrrm] pentads are always greater than the [rmrm] pentad. The process (Patent Claim 11) according to the invention is specifically characterised in that a specially selected catalyst combination is used, containing, on the one hand, a specific, exactly defined metal complex and, on the other hand, an activator.

The metal complex is a metallocene compound. Herewith, metal compounds of the Fourth Auxiliary Group of the Periodic System Table IVB generally come into question, which compounds may be present as defined metal complexes and with which compounds activators are mixed. In general, the metals are present in the complexes in formally positively charged manner.

As regards the metals, titanium, zirconium, hafnium, vanadium, niobium, and tantalum specifically come into question, the metal atom preferably showing halogen or a C_1 - C_8 alkyl, aryl or benzyl as residue X.

The metallocene compound which is suited for preparing the linear, isotactic polymers according to Patent Claim 11 is defined by general Formula I.



(I)

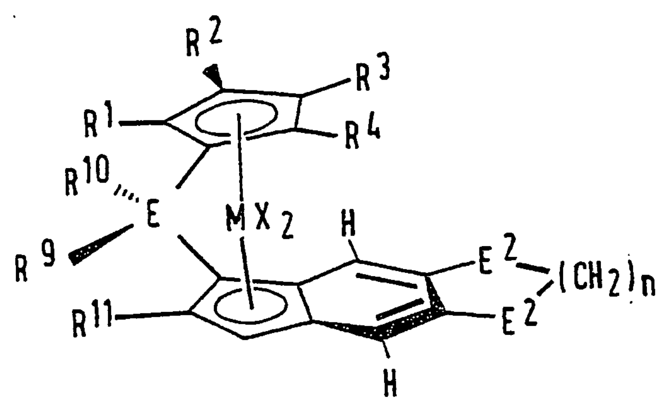
wherein the residues R^1 - R^7 are a linear or branched C_1 - C_{10} alkyl, a 5-7-linked cycloalkyl that, in its turn, may carry one or several C_1 - C_6 alkyl residues as substituents, a C_6 - C_{18} aryl, aryl alkyl or alkyl aryl, in which case R^1, R^2; R^3, R^4; and R^6, R^7, here again, my be partially or simultaneously integrated into 5-7-linked cycloalkyl or aryl rings fused thereto.

In case of the metallocene compound according to general Formula I, it is essential that, in general Formula I, the carbon atom adjacent to the residue R^7 and the carbon atom adjacent to the residue R^6 be, with the indene ring system, only hydrogen. Thereby, it is ensured that, with the indene ring system, a linear system can form by the residues R^6 and R^7 , which system, obviously, will prove to be especially advantageous when preparing the isotactic elastomers according to the invention. In contrast to the metallocene complex according to European Printed Publication 0 707 016 A1, only hydrogen atoms and no

carbon atoms with further residues, as is imperative in the aforementioned European laying-open specification, can, thus, be found at the positions mentioned in the aforegoing.

In this connexion, suitable bridging structural units E are 1.2-ethyl, 1.3-propyl, 1.4-butyl, carbon, silicon or germanium. For the case that E is carbon, silicon or germanium, the bridging structural unit E may, herewith, additionally carry the residues R^9 and R^{10} which, then, are a C_1 - C_8 alkyl, a 4-7-linked cycloalkyl or aryl, R^9 and R^{10} being able to also form a 4-7-linked cycloalkyl or aryl jointly with E.

A particularly preferred embodiment of the invention resides in that such a metallocene complex is used as reflected by general Formula VII.



(VII)

wherein all the residues have the significations indicated above. In contrast to the metallocene complex according to general Formula I, it, however, now is imperative here on the indene ring system that another ring fused thereto be at hand which is bridged via two E^2 groups.

E_2 therewith signifies CH_2, oxygen or sulphur and n is 1 or 2.

As defined in Patent Claim 11, it certainly is furthermore provided in accordance with the invention, to additionally use at least also one activator, apart from the metallocene compounds specified above. The invention, herewith, generally encompasses all the activators that have as yet become known in the state-of-the-art for metallocene compounds. Such activators have also been specified by European Printed Publication 0 707 016 A1. As activator, at least one compound of general Formulas II to VI is, however, used with special preference. Accordingly, the activator may be an open-chain or cyclic alumoxane compound of general Formula II or III, such as is reflected hereinafter:

$$-(\overset{R^8}{\overset{|}{Al}}-O-)_n- \quad (II) \qquad \qquad \boxed{(\overset{R^8}{\overset{|}{Al}}-O-)_n} \quad (III)$$

wherein R^8 is a C_1 - C_4 alkyl group and n is a number between 5 and 30.

In case of the catalyst combination according to the invention, also the above-specified compounds of general Formulas II and III can, alone or in combination with the subsequent activators such as are reflected by general Formulas IV to VI, be used.

$$B(C_6F_5)_3 \quad (IV) \qquad R^9{}_3C[B(C_6F_5)_4] \quad (V)$$

$$[R^9{}_3NH][B(C_6F_5)_4] \quad (VI)$$

In general Formulas IV to VI, R^9, in this connexion, signifies a $C_1 - C_4$ alkyl group or an aryl group.

It has, therewith, proven to be especially favourable when the metallocene complex according to general Formula I and the activator according to general Formulas II to VI are employed in such quantities that the atomic ratio between aluminium from the alumoxane or boron from the cationic activator and the transition metal from the metallocene complex is within the range of from 1:1 to 10^6:1.

Pressures of from 1 to 100 bars, preferably of from 3 to 20 bars and in particular of from 5 to 15 bars, have proven to be suitable reaction parameters for preparing the linear, thermoplastic, elastomeric olefin polymers. Favourable temperatures are within the range of from -50 °C to 200 °C, of preference at from 100 to 150 °C and of high preference at from 20 to 50 °C.

The polymerisation reactions can be carried out in the gas phase, in suspension and in supercritical monomers and especially in solvents inert under polymerisation conditions. In particular the solution polymerisation has proven to be the clearly superior thing for the present preparation process. Suitable inert solvents for that purpose are such solvents that do not contain any reactive groups in the molecule, i. e. aromatic solvents like benzole, toluol, xylol, ethyl benzole or alkanes such as e. g. propane, n-butane, i-butane, pentane, hexane, heptane or mixtures thereof.

The polymers according to the invention are particularly suited for the making of fibres, sheets, and moulded bodies and highly suited for such application cases that make impact resistance a

precondition. The polymers according to the invention can, furthermore, be utilised as blend components in plastic materials, especially in such plastic materials that are to be of the impact resistant kind.

The present invention will, hereinafter, be explained in more detail on the basis of several preparation examples of the catalysts and on the basis of polymerisation examples. Herewith, there show:

Fig. 1 tensile-strength measurements on two polymers according to the invention, as compared to two polymers from European Printed Publication 0 707 016 A1,

Fig. 2 an X-ray structure analysis of a metallocene complex according to the invention,

Fig. 3 a nuclear magnetic resonance (NMR) spectrum of a polymer according to the invention, and

Fig. 4 a nuclear magnetic resonance (NMR) spectrum of another polymer according to the invention.

Fig. 1 now illustrates the tensile-strength measurements of two selected examples from European Printed Publication 0 707 016 A1, as compared to two polymers prepared in accordance with the invention. By the remarks "Cf. Fig. 4" and "Cf. Fig. 5" in Fig. 1, the corresponding examples from European Printed Publication 0 707 016 A1 are meant in this case. As can be drawn from a comparison of those tensile-strength curves with the tensile-strength curves of the polymers (PP 36 and PP 45) prepared according to

the invention, the polymers according to the invention show a distinctive, rubber-elastic plateau. Contrary thereto, the polymers according to European Printed Publication 0 707 016 A1 present either a flow behaviour (Fig. 4) or the polymer breaks in case of higher expenditures of force (Fig. 5). It is just that comparison that clearly illustrates the surprising characteristics of the polymers prepared according to the invention and showing a distinctive, rubber-elastic behaviour.

Catalyst preparation

Obtaining of 5.6-cyclopenta-2-methyl-indane-1-one

40.4 mL of methacryl acid chloride (387.9 mmols) are, together with 62.06 gms of anhydrous aluminium chloride (20 mol% in excess), incorporated into 250 mL of CH_2Cl_2, cooled down to -78 °C, and slowly mixed with 50.0 mL of indane (45.84 gms, 387.9 mmols). As the indane is added, the colour changes from bright yellow to orange. The mixture is carefully quenched with diluted HCl*aq, washed with hydrous K_2CO_3 solution and water, and dried through Na_2SO_4.

Yield: 70.07 gms (376.2 mmols) of oily product, 97.0 % of the theory NMR (200 mcps, CDCl3 7.24 ppm): δ 1.25 ppm d (J = 6.9 cps) 3 H methyl group, δ 2.10 ppm m (J = 3.7 to 7.6 cps) 2 H aliphatic protons of the cycles, δ 2.62 ppm m 2 H aliphatic protons of the indanone ring, δ 2.86 ppm m (J = 11 to 14 cps) 4 H aliphatic protons of the cycles, δ 3.25 ppm m (J = 7.0 cps) 1 H aliphatic proton of the indanone system, δ 7.21 and 7.51 ppm s 2 H aromatic MS (GC-MS) m/z 186 (M+ 100 %), (186, 251 mol-1).

Obtaining of 5.6-cyclopenta-2-methylindane-1-ole

70.07 gms (376.2 mmols) of the 2-methyl-5.6-cyclopentylindane-1-one are, with 5 gms of $LiAlH_4$, reduced in 200 mL of Et_2O by letting the ketone drip (2 hrs) slowly towards an ice-cooled suspension of $LiAlH_4$. Agitating is effected all through the night and quenching with H_2O is carried out, the colour of the solution changing from lime green to bright yellow. Now 15 mL of HCl are added in concentrated manner and the emulsion is agitated for 1 h. The etherial phase is separated, neutralised with 200 mL of K_2CO_3 solution, and three times washed with water. Thereafter, drying is effected through Na_2SO_4 and the solvent is completely removed. A crystalline mixture of the diastereomeric 1-indanoles is obtained. NMR (200 mcps, $CDCl_3$): δ 1.13 ppm d 3 H methyl group, δ 1.76 ppm wide 1 H OH group, δ 2.05 ppm m 2 H aliphatic protons of the cycles, δ 2.15 to 2.71 ppm m 2 H aliphatic protons of the indanole ring, δ 2.87 ppm m 4 H aliphatic protons of the cycles, δ 3.08 ppm 1 H aliphatic proton of the indanole system, δ 4.17 and 4.93 ppm d 2 H with OH function on the indanole ring, δ 7.08 and 7.23 ppm d 2 H aromatic.

Yield: 69.62 gms, 369.8 mmols, 98.3 % of the theory
MS (GC-MS) m/z 188 (M+ 100 %), (188.267 gms mol^{-1}).

Obtaining of 5.6-cyclopenta-2-methylindene

69.62 gms (369.8 mmols) of the diastereomer mixture of the 2-methyl-5.6-cyclopentylindene-1-oles are dissolved in 500 mL of benzole; and then 3 to 5 gms of p-TosOH are added and the emulsion is, for three quarters of an hour, boiled on the water separator under reflux. The organic phase is separated,

neutralised with 200 mL of K_2CO_3 solution, and three times washed with water. Thereafter, drying is effected through Na_2SO_4 and the solvent is completely removed.

The product colourlessly crystallises from n-pentane; yield: 57.67 gms, 338.7 mmols corresponding to 91.6 % of the theory MS (GC-MS) m/z 170 (M+ 100 %), (170.225 gms mol^{-1}). NMR (200 mcps, CDC13 7,24 ppm): δ 2.23 ppm m/s 5 H methylene and 2-methyl group of the indene system, δ 3.01 ppm t 4 H methylene groups, δ 3.32 ppm s 2 H methylene group acids, δ 6.51 ppm s 1 H olefinic indene system, δ 7.20 and 7.34 ppm s 2 H aromatic, 13-NMR (200 mcps, $CDCl_3$): δ 16.8 ppm methyl group, δ 25.8 ppm methylene group of Cycle 5, δ 32.66 and 32.72 ppm methylene groups of the Cycle, δ 42.2 ppm methylene group of the indene system, δ 127.1 ppm tertiary C-atom of the indene system, δ 115.5 and 119.5 (each with H) ppm aromatic C-atoms, the same without H for 139.6, 141.7, 142.1, 144.4, and 145.0 ppm incl 4° olefinic C-atom of the indene system (cf. CH correlation and HH-COSY).

Obtaining of 1-(9 fluorenyl)-2(1-(5.6-cyclopenta-2-methyl)indenyl)ethane

3.89 gms of 2-methyl-5.6-cyclopentylindene-1 (22.85 mmols) are, with 14.3 mL of n-BuLi, deprotonated in 150 mL of dioxane and then mixed with a solution of 25.13 mmols of 2-(9'-fluorenyl)ethyltrifluoromethane sulphonate in 100 mL of dioxane. Agitating is effected all through the night, heating up to 60 °C is carried out for half an hour and the solution is quenched with ca. 3 mL of H_2O. The dioxane is removed and the product is extracted with three times 200 mL of Et_2O. Without chromatographic processing, 6.49 gms

(17.9 mmols, 78.3 % of the theory) of a colourless, crystalline Product are obtained.

NMR (200 mcps, CDC13, 7.24 ppm): δ 1.89 ppm s 3 H methyl group, δ 1.41 ppm to 1.72 ppm m 4 H aliphatic protons of the bridge, δ 2.10 ppm pseudo-t 2 H aliphatic protons of the cycle, δ 2.90 ppm pseudo-t 4 H aliphatic protons of the cycle, δ 3.87 ppm t 1 H aliphatic proton of the fluorene system, δ 6.40 ppm s 1 H indene proton, δ 6.98 and 7.07 ppm aromatic protons of the indene system, δ 7.31 to 7.77 ppm m 8 H aromatic of the fluorene. MS (FD) m/z 362.5 (M+ 100 %).

Obtaining of 1-(9 fluorenyl)-2-(1-(5.6-cyclopenta-2-methyl) indenyl)ethane zirconocene dichloride

1.711 gms of 1-[1'-(2'-methyl)5', 6'-cyclopentylindenyl-2-(9"-fluorenyl)] ethane (4.72 mmols) are dissolved in 100 mL of toluol, mixed with 10 mL of dioxane, and deprotonated, at low temperature, with 5.9 mL of n-BuLi. Agitating is effected for ca. 1 hour and then the suspension is again cooled down to -78 °C. Now 1.10 gm of $ZrCl_4$ is added. That suspension is agitated, at room temperature, for another 14 hours, in which case a fine red powder forms that can be crystallised after a separation of formed LiCl from toluol.

Yield: 2.148 gms (4.11 mmols, 87.1 % of the theory). NMR (500 mcps, $C_2D_2Cl_4$ 80 °C); δ 2.00 ppm m 2 H methylene group cyclopentane ring (J = 6.8 to 7.5 cps), δ 2.15 ppm s 3 H methyl group, δ 2.79 to 2.94 ppm m 4 H methylene groups cyclopentane ring adjacent to the aromatic system (J = 7.5 to 9.7 cps), δ 4.05 ppm m (J = 3.5 to 13.2 cps) 2 H aliphatic protons of

the bridge (in case of the fluorene), δ 3.83 and 4.57 ppm m (J = 4.2 to 10.0 cps) 1 H aliphatic protons of the bridge (diastereotopic) at a time, δ 6.05 ppm s 1 H indene proton, δ 7.03 to 7.85 ppm m 10 H aromatic.

MS (El) m/z 5, 22, 6 isotopic pattern corresponding to natural distribution.

EA CH-combustion analysis: calculated 64.35 % C 4, 63 % H

Found: 64.08/63.89 % 4.53/4.63 %

Polymerisation example

All the polymerisations were carried out in 300 mL of toluol under the conditions indicated in Table 1.

The NMR data were measured by means of a Bruker AMX 500 device and evaluated on the basis of literature data.

Table 1

Run No.	Catalyst	Amount#	Tp [°C]	C3 [moll-1]	Yield [g]	tp [min]	Activity*	Tg [°C]	Tm [°C]	Mw	Mw/Mn
P 36	Flu-Et-IInd	7,5	30	2,9	36,87	33	3080	-5,9	50,2	171.000	1.96
P 45	Flu-Et-IInd	10	35	4,92	115,23	39	3603	-7,5	51,7	95.700	1.74
Run No.	Pentaden in %	mmmm	mmmr	rmmr	mmrr	mmrm+rmrr	rmrm	rrrr	rrrm	mrrm	Al/Zr
P 36		36,7	18,5	2,1	21,1	5,0	0,0	2,5	3,7	10,3	2000
P 45		36,5	17,9	1,7	21,0	5,8	0,3	3.1	3.6	10,1	2000
	#in µmol		*kgPP/mol[Zr]mol[C3]h								

Claims

1. Linear, isotactic polymer which has a structure of one or several C_2 to C_{20} olefins and of which the isotacticity, due to a statistic distribution of stereoscopic errors in the polymer chain, is within the range of from 25 to 60 % of [mmmm] pentad concentration with the proviso that an arbitrary or rather regular sequence of isotactic and atactic blocks is excluded, the polymer having a mean molecular weight Mw within the range of from 100,000 to 800.000 gms/mol and a TG of from -50 to +30.

2. Isotactic polymer according to Claim 1, characterised in that the [rmrm] pentad amounts to a maximum of 2.5 % of the entire pentad area and each of the [rrrr] and [mrrr] pentads is greater than the [rmrm] pentad.

3. Isotactic polymer according to Claim 1 or 2, characterised in that the polymer has a thermoplastic-elastic behaviour.

4. Linear, isotactic polymer according to at least one of Claims 1 to 3, characterised in that the olefin is a C_3 to C_{20} alk-1-ene.

5. Isotactic polymer according to Claim 4, characterised in that the alk-1-ene is selected from propene, 1-butene, 2-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-hexadecene, 1-octadecene, 1-eicosene.

6. Isotactic polymer according to at least one of Claims 1 to 3, characterised in that the olefin is a C_5 to C_{20} cycloolefin.

7. Isotactic polymer according to Claim 6, characterised in that the cycloolefin is selected from cyclopentene, cyclohexene, norbonene and its derivatives.

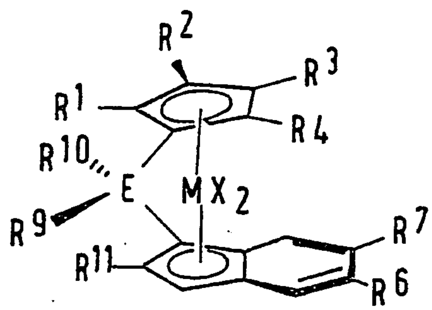
8. Isotactic polymer according to at least one of Claims 1 to 7, characterised in that it is polypropylene.

9. Isotactic polymer according to at least one of Claims 1 to 7, characterised in that it is a copolymer having a structure of propylene and a C_4 - C_{20} olefin and/or cycloolefin.

10. Isotactic polymer according to at least one of Claims 1 to 7, characterised in that it is a

terpolymer having a structure of propylene, C_2 - C_{20} olefin and a cycloolefin.

11. Process for preparing linear, isotactic polymers which have a structure of at least one monomer of a C_2 to C_{20} olefin and of which the tacticity varies within the range of between 25 and 60 % of [mmmm] pentad concentration, an arbitrary or rather regular sequence of isotactic and atactic blocks being excluded, in which process a C_2 to C_{20} olefin and an activator are reacted in the presence of a catalyst combination containing a metal complex of general Formula I



(I)

wherein the substituents have the following significations:

R_1 - R_7 linear or branched C_1 to C_{10} alkyl, 5- to 7-linked cycloalkyl which, in its turn, can carry one or several C_1 to C_6 alkyl residues as substituent, C_6 to C_{18} aryl or arylalkyl or alkylaryl, in which case R^1/R^2, R^3/R^4, R^6/R^7 can be partially or simultaneously integrated into 5- to 7-linked cycloalkyl or aryl rings fused thereto;

R^9, R^{10} — C_1 to C_8 alkyl, 4- to 7-linked cycloalkyl, aryl, in which case R^9,R^{10} can, jointly with E, form a 4- to 7-linked cycloalkyl or aryl;

R^{11} — C_1 to C_8 alkyl, aryl, C_1 to C_8 oxyalkyl, C_1 to C_8 trialkylsiloxy;

M — titanium, zirconium, hafnium, vanadium, niobium, tantalum;

X — halogen or C_1 to C_8 alkyl, aryl, benzyl;

E — carbon, silicon, germanium or 1.2-ethyl, 1.3-propyl, 1.4-butyl.

12. Process according to Claim 11, characterised in that the activator is an open-chain or cyclic alumoxane compound of general Formula II or III

$$-\!\!\!-(\overset{\overset{R^8}{|}}{\mathrm{Al}}-\mathrm{O}-)_n-\!\!\!- \quad (\mathrm{II}) \qquad \boxed{(\overset{\overset{R^8}{|}}{\mathrm{Al}}-\mathrm{O}-)_n} \quad (\mathrm{III})$$

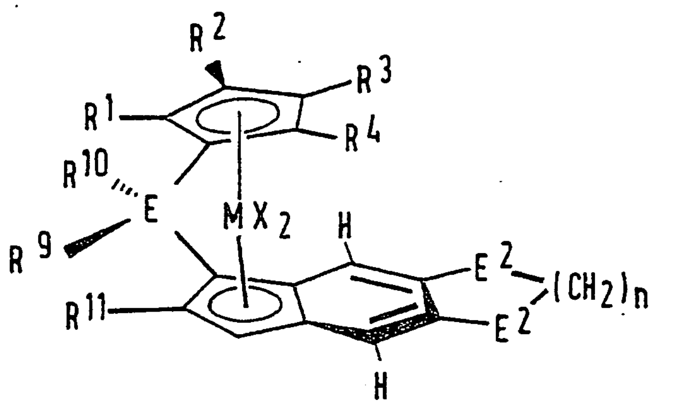
R^8 standing for a C_1 to C_4 alkyl group and <u>n</u> standing for a number between 5 and 30, and/or a cationic activator of general Formulas IV to VI

$$B(C_6F_5)_3 \quad (IV) \qquad R^9{}_3C[B(C_6F_5)_4] \quad (V)$$

$$[R^9_3NH][B(C_6F_5)_4] \quad (VI)$$

R^9 signifying a C_1 to C_4 alkyl group or an aryl group.

13. Process according to Claim 11 or 12, characterised in that the metal complex according to general Formula I preferably is a compound of general Formula VII.



(VII)

wherein the residues R^1 to R^{11} have the significations indicated in general Formula I and $E^2 = CH_2$, O or S and n = 1 or 2.

14. Process according to at least one of Claims 11 to 13, characterised in that the metallocene complex of general Formula I and the activator according to general Formulas II to VI are utilised in such quantities that the atomic ratio between aluminium from the alumoxane and/or boron from the cationic activator and the transition metal from the metallocene complex is within the range of from 1:1 to 10^6:1.

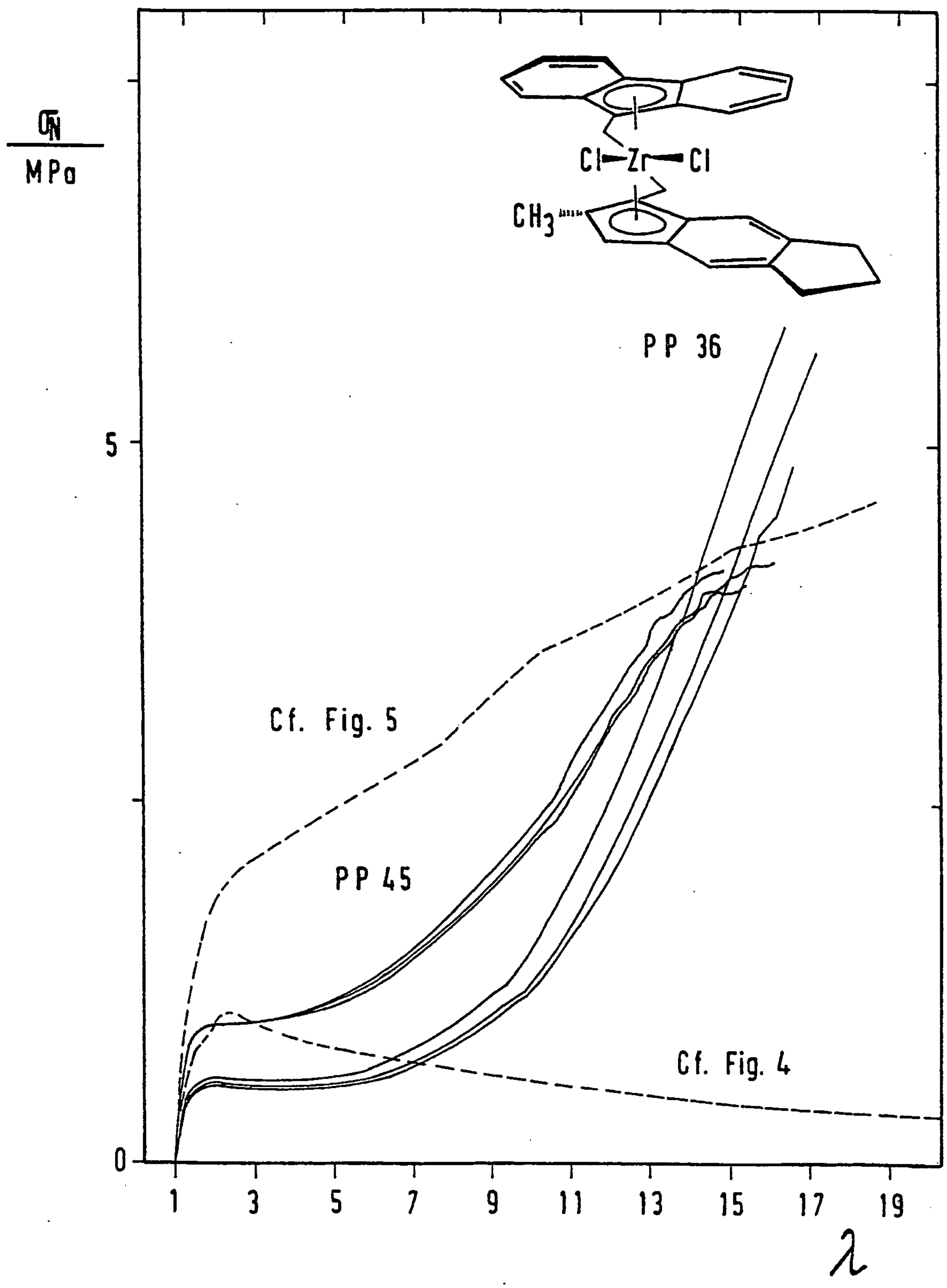
15. Process according to at least one of Claims 12 to 14, characterised in that the polymerisation reaction is carried out in the gas phase, in suspension or in supercritical monomers, especially in solvents inert under the polymerisation conditions.

16. Process according to at least one of Claims 12 to 15, characterised in that, as inert solvents, solvents are used that do not contain any reactive molecules, such as e. g. benzole, toluol, xylol, ethyl benzole or alkanes such as e.g. propane, n-butane, i-butane, pentane, hexane, heptane or mixtures thereof.

17. Process according to at least one of Claims 12 to 16, characterised in that polymerisation is carried out at pressures of from 1 to 100 bars, preferably from 3 to 20 bars and especially from 5 to 15 bars, and at temperatures of from -50 to 200 °C, of preference from 10 to 150 °C and especially at from 20 to 40 °C.

18. The use of the isotactic polymers according to at least one of Claims 1 to 11 for making fibres, sheets, and moulded bodies or as impact resistance modificator in polymers.

FIG.1



σ_N / MPa
5
0
1
3
5
7
9
11
13
15
17
19
λ
Cl
Zr
Cl
CH3
PP 36
PP 45
Cf. Fig. 5
Cf. Fig. 4

FIG.2

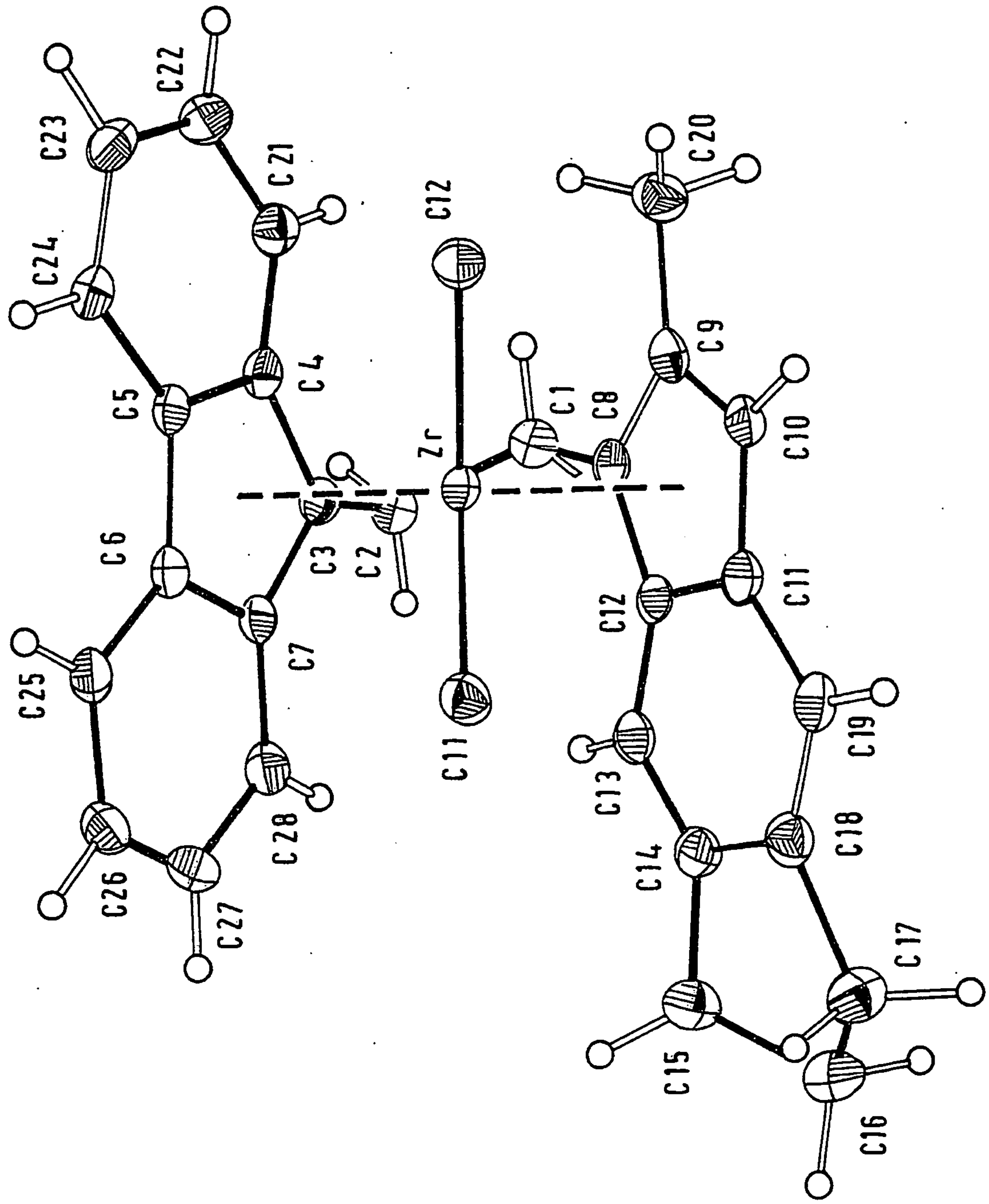

C22
C23
C21
C20
C12
C24
C9
C4
C5
C1
C8
Zr
C10
C6
C3
C2
C12
C11
C7
C25
C11
C19
C13
C28
C18
C14
C26
C27
C17
C15
C16

FIG.3

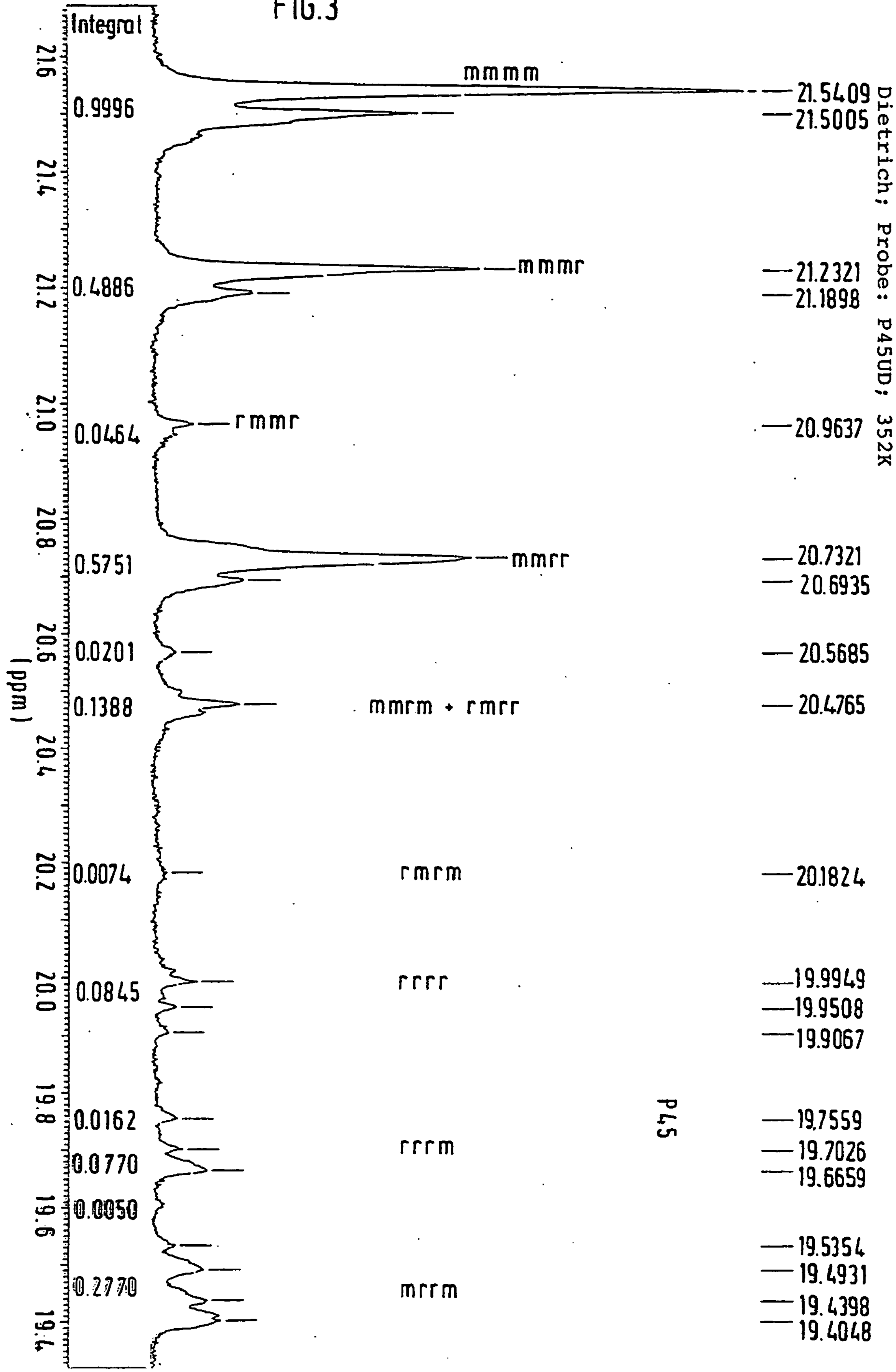
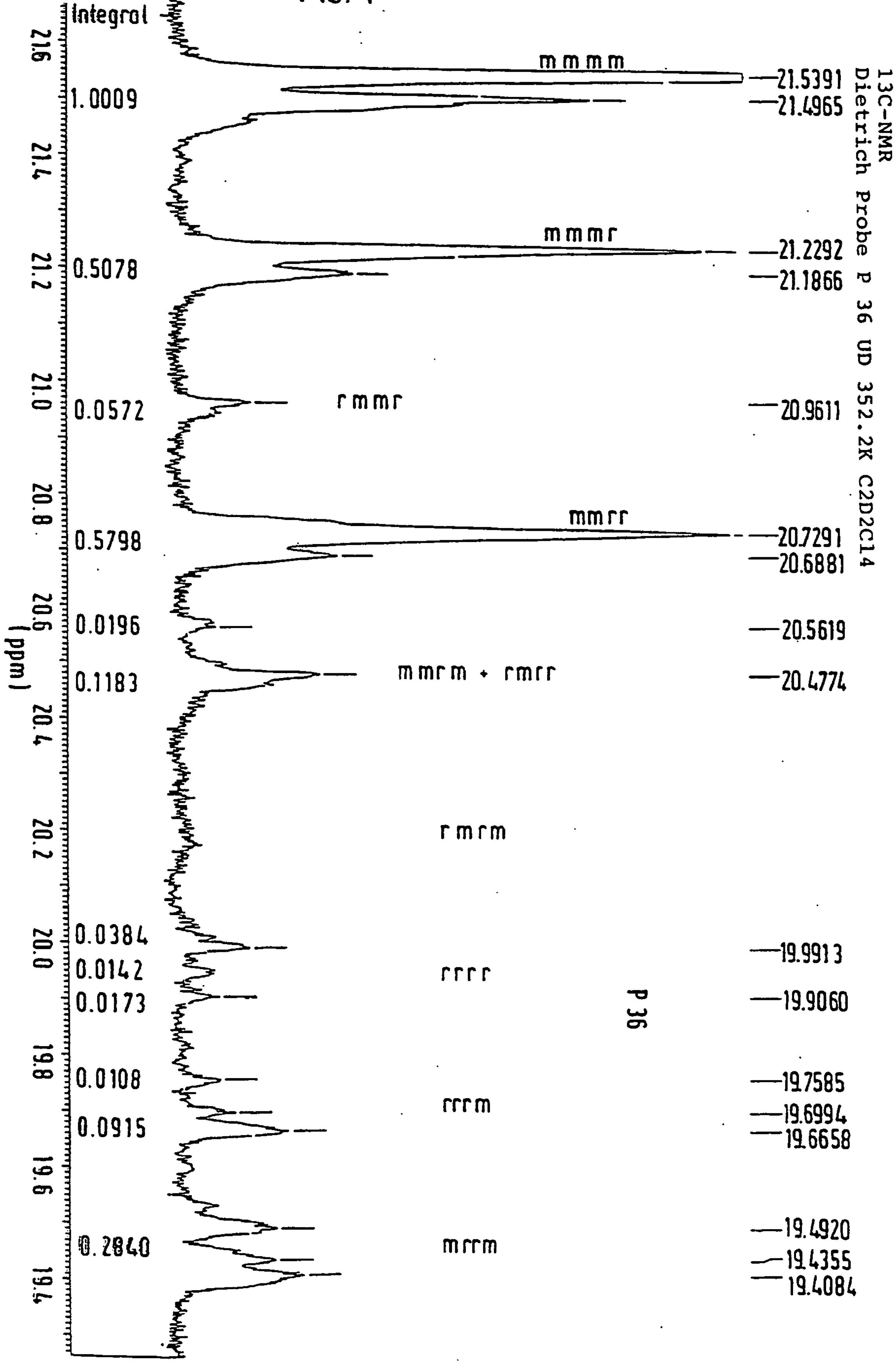

Integral
0.9996
0.4886
0.0464
0.5751
0.0201
0.1388
0.0074
0.0845
0.0162
0.0770
0.0050
0.2770
21.6
21.4
21.2
21.0
20.8
20.6
20.4
20.2
20.0
19.8
19.6
19.4
(ppm)
mmmm
mmmr
rmmr
mmrr
mmrm + rmrr
rmrm
rrrr
rrrm
mrrm
P45
21.5409
21.5005
21.2321
21.1898
20.9637
20.7321
20.6935
20.5685
20.4765
20.1824
19.9949
19.9508
19.9067
19.7559
19.7026
19.6659
19.5354
19.4931
19.4398
19.4048
Dietrich; Probe: P45UD; 352K

FIG. 4


13C-NMR
Dietrich Probe P 36 UD 352.2K C2D2Cl4
Integral
(ppm)
21.6
21.4
21.2
21.0
20.8
20.6
20.4
20.2
20.0
19.8
19.6
19.4
1.0009
0.5078
0.0572
0.5798
0.0196
0.1183
0.0384
0.0142
0.0173
0.0108
0.0915
0.2840
mmmm
mmmr
rmmr
mmrr
mmrm + rmrr
rmrm
rrrr
rrrm
mrrm
P 36
21.5391
21.4965
21.2292
21.1866
20.9611
20.7291
20.6881
20.5619
20.4774
19.9913
19.9060
19.7585
19.6994
19.6658
19.4920
19.4355
19.4084

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/02379

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/06 C08F232/00 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DIETRICH, ULF ET AL: "Control of Stereoerror Formation with High-Activity "Dual-Side" Zirconocene Catalysts: A Novel Strategy To Design the Properties of Thermoplastic Elastic Polypropenes" J. AM. CHEM. SOC. (1999), 121(18), 4348-4355 , XP002110148 page 4349, compound 15 page 4351, table 2 entries 26, 28 and 31 page 4354 ---	1-5,8, 11-17
P,X	RIEGER, BERNHARD ET AL: "Novel metallocene catalyzed polypropene homo- and brush-copolymers: control of new morphologies and beyond" POLYM. MATER. SCI. ENG. (1999), 80, 51-52 , XP002110149 the whole document --- -/--	1,3-5,8, 11-13, 15,17

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 July 1999	17/09/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Gamb, V

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Ir ational Application No
PCT/EP 99/02379

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	DIETRICH U ET AL: "NEW CLASS OF THERMOPLASTIC ELASTIC POLYPROPENES PREPARED WITH A HIGH ACTIVITY 'DUAL SIDE' ZIRCONOCENE CATALYST" RAPRA ABSTRACTS, vol. 36, no. 1, January 1999 (1999-01), page 138 XP000800737 ISSN: 0033-6750 abstract	11-13
A	RIEGER B: "STEREOSPECIFIC PROPENE POLYMERIZATION WITH RAC- 1,2-BIS(N5 -(9OFLUORENYL))-1-PHENYLETHANEZIRCONIUM DICHLORIDE/METHYLALUMOXANE" POLYMER BULLETIN, vol. 32, no. 1, 1 January 1994 (1994-01-01), pages 41-46, XP000420835 ISSN: 0170-0839 page 43 page 45; examples 3,5; table 2	1-5,8, 11-17
A	EP 0 747 406 A (FINA TECHNOLOGY) 11 December 1996 (1996-12-11) page 9; example 5; tables 3,4	1,2,4,5, 8
A	WO 96 20225 A (MONTELL TECHNOLOGY COMPANY BV) 4 July 1996 (1996-07-04) abstract page 33; examples 1-6; table 1	1,4,5,8
P,A	DE 197 09 486 A (STUDIENGESELLSCHAFT KOHLE MBH) 10 September 1998 (1998-09-10) examples 3,4 page 8, tables	1,2,4,5, 8,18
E	WO 99 20664 A (MINNESOTA MINING & MFG) 29 April 1999 (1999-04-29) abstract page 37; example 12 page 30, line 4 - line 5 claim 1	1-5,8,18

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/02379

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			DE	69600747	D	12-11-1998
			DE	69600747	T	08-04-1999
			ES	2123316	T	01-01-1999
			JP	9136930	A	27-05-1997
WO 9620225	A	04-07-1996	IT	MI942566	A	20-06-1996
			IT	MI942567	A	20-06-1996
			CA	2183419	A	04-07-1996
			CN	1147822	A	16-04-1997
			EP	0745099	A	04-12-1996
			JP	9509982	T	07-10-1997
			US	5747621	A	05-05-1998
DE 19709486	A	10-09-1998	WO	9839369	A	11-09-1998
WO 9920664	A	29-04-1999	NONE			